

UDC 666.11.01:666.113.28'27'

THE EFFECT OF BIVALENT CATIONS ON THE PHYSICOCHEMICAL PROPERTIES AND STRUCTURE OF BOROSILICATE GLASSES

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Translated from *Steklo i Keramika*, No. 3, pp. 8 – 11, March, 2004.

The effect of modifier oxides (MgO, CaO, SrO, BaO, and ZnO) introduced instead of SiO₂ into borosilicate glass on glass properties is investigated. It is established that the physicochemical properties (TCLE, softening temperature, microhardness, density, water resistance) of glasses are determined mainly by structure and phase composition and, to a lesser extent, depend on the type of modifier oxide.

The most common compositions used in vitreous coatings for ceramics, microsphere glass, and other glasses are borosilicate compositions containing B₂O₃ ranging from 5 to 30% (here and elsewhere mass content). These compositions, as a rule, contain various modifier oxides, which jointly impart the required properties to glass.

Oxides of bivalent metals introduced in borosilicate glasses modify their properties within a wide range. One of the main reasons for this effect is believed to be the modification of the structural state of boron depending not only on the quantitative ratio between R₂O, RO, and B₂O₃, but also on the nature of monovalent and bivalent metals (R₂O — Na₂O, K₂O; RO — MgO, CaO, SrO, BaO, ZnO). Such bivalent oxides have a substantial effect on phase separation in glasses, which merits special investigation.

The present study considers the effect of Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, and Zn²⁺ cations on modifying the physicochemical properties of glasses with respect to their structure and phase composition.

The studies were performed on systems containing (%): 10Na₂O, xRO, yB₂O₃, zSiO₂. The values *x* for CaO and ZnO varied from 5 to 30%, for MgO and SrO from 2.5 to 10%, and for BaO from 5 to 20%. The values *y* varied from 5 to 50%, and the values *z* from 30 to 75%. The content of all oxides varied with an interval of 2.5%.

The investigation of melting and working properties of the glasses indicated that the compositions are technologically suitable, and their melting proceeds in a temperature range of 1400 – 1450°C. The working viscosity of melts varies insignificantly and is determined by the bivalent cation radius. Thus, the magnesium-bearing glasses have the lowest working viscosity. They also have the smallest temperature interval for decreasing viscosity. In general the effect of RO oxides on lowering viscosity and, accordingly, on increasing

melting duration is ranked in the following sequence: BaO < SrO < CaO < ZnO < MgO.

It is established that clear glasses prevail in the specified systems; there are as well small areas of opalescent compositions for the calcium and zinc-bearing systems. Furthermore, the calcium-bearing system has opacified and opal glasses with a CaO content below 25%. At the same time, this area narrows for high-silica compositions (over 50% SiO₂) and corresponds to about 10% CaO. The opal glass boundary in the zinc-bearing system corresponds to 10% ZnO in the range of high-silica compositions and to 35% ZnO for compositions bearing less than 35% SiO₂.

An electron-microscope study of opal and opacified glass revealed the liquation nature of their phase separation; in most cases it was drop liquation. The drops are distributed uniformly and are separated by interlayers of the matrix vitreous phase. The number of drops per surface area unit and the drop size change depending on the glass composition. The largest drops (above 1 μm) are typical of calcium-bearing glasses, whereas the sizes of liquation heterogeneities in zinc-bearing glasses are significantly smaller (0.05 – 0.50 μm). All the glasses considered are x-ray-amorphous.

Local x-ray-spectral analysis of elemental composition using a Camebax electron microanalyser produced by Cameca (France) [1] was used to identify the composition of phases in liquating glasses. To study calcium-containing liquation compositions, drops of size 2.0 – 2.5 μm were grown by protracted heat treatment of glass for 24 h at a temperature of 750 – 800°C. It was found that with 10 – 20% content of CaO the glass matrix is rich in SiO₂ and the drops contain CaO, Na₂O, and presumably B₂O₃. In glasses containing over 20% CaO the matrix is formed with a phase rich in B₂O₃, CaO, and Na₂O, whereas SiO₂ is mostly concentrated in the drop phase.

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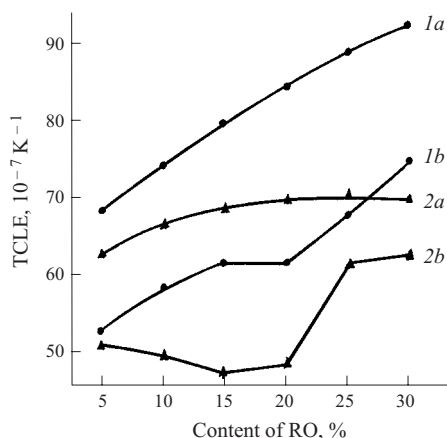


Fig. 1. Dependence of TCLE on content of CaO (1) and ZnO (2): a) calculated values; b) experimental data.

Glasses of the zinc-bearing system have metastable liquation and the sizes of emerging drops are very small. Protracted (36 h) heat treatment at 750°C made it possible to grow drops of size 2.0–2.2 μm , which were analyzed. With a ZnO content below 20% the matrix of zinc-bearing glasses is high-silica; B_2O_3 is presumably concentrated in drops. The drops contain ZnO and Na_2O , but part of these oxides still remains in the matrix. Thus, with increasing content of the modifier oxides (CaO and ZnO), we observe an inversion of the liquation phases in the transition from high-silica to low-silica glasses.

The study of calcium and zinc-bearing glasses using the method of electron paramagnetic resonance established that as the volume of the silica-rich phase grows, the spectrum intensity of three-coordination boron increases. With increasing volume of the phase containing B_2O_3 , CaO, and Na_2O in calcium-bearing glasses and the phase containing ZnO, B_2O_3 , and Na_2O in the zinc-bearing system, boron has coordination 4. In glasses existing outside liquation areas, 3-coordination boron prevails. In zinc-bearing glasses, apart from paramagnetic centers related to boron nuclei, paramagnetic centers related to the free electron in zinc are identified as well. Zinc in the high-silica phase is present mostly in 4-coordination, which corroborates the probability of its incorporation in the silicon-oxygen skeleton, and in the boron-rich phase it exists in 6x-coordination.

The determination of the dependence of physiochemical properties of glasses on their composition is essential for the specified systems due to their liquation. Accordingly, analysis of their properties has to take into account the coexistence of two vitreous phases of different compositions in glass, and the results should be interpreted based on the dependence of the properties of two-phase systems on the constituent phases.

One of the main service properties of glasses is the TCLE, whose values are determined mostly by the strength of the bonds between the structural elements, the forces of

their interaction, and the packing density. A decrease in the specified structural characteristics increases the TCLE of glasses. It is known that the TCLE of single-phase glasses [2] depends additively on a glass composition, and this dependence for liquating compositions becomes more complicated.

The results of experimental determination of TCLEs of calcium-bearing glasses indicate that their values vary from 52×10^{-7} to $74 \times 10^{-7} \text{ K}^{-1}$ and increase with increasing CaO content. Figure 1 clearly exhibits two inflections on the curve of the dependence of TCLE of experimentally measured calcium-containing glasses on their composition, whereas this dependence for TCLE theoretically calculated using A. A. Appen's method [1] represents a straight line. With a 15–20% content of CaO an inflection is registered on the curves of the dependence of experimental TCLE values on the composition. This regularity can be explained arguing that the matrix makes the most significant contribution to the TCLE under drop liquation, and isolated inclusions play a smaller role. With a CaO content below 20% the matrix is formed by the high-silica phase, which typically has lower TCLE values. When the CaO content increases above 20%, an inversion of the phases is registered. In this case the matrix contains B_2O_3 , CaO, and Na_2O , which leads to a perceptible increase in the TCLE of glasses. The measured TCLE values in all cases are significantly below the calculated values.

In zinc-bearing glasses the TCLE varies from 48×10^{-7} to $62 \times 10^{-7} \text{ K}^{-1}$. It should be noted that TCLE values in these glasses are lower than those of analogous calcium-bearing glasses. This is due to the difference between the partial numbers of the oxides introduced. In zinc-bearing glasses there are two inflections as well on the curve of the dependence of experimentally measured TCLE values on the composition in the range of 20–25% ZnO.

Thus, with a 20% or lower content of ZnO the matrix is high-silica, which perceptibly decreases the TCLE of zinc-bearing glasses. With a ZnO content higher than 20%, the matrix is formed by the sodium-borate phase, which causes a significant increase in the experimental TCLE value. In both cases the estimated values of TCLE are above the experimental values, which is related to liquation phenomena in glasses. One should note that TCLEs of glasses in the zinc-bearing system are lower than those in the calcium-bearing system.

Experimental determination of TCLE of clear magnesium-, strontium-, and barium-containing glasses indicates that an increase in the content of BaO, SrO, and MgO in the range considered contributes to increasing the TCLE. The lowest TCLE values can be reached by introducing MgO, and higher values are achieved by introducing SrO and BaO. A correlation of experimental and calculated data established that the discrepancy in TCLE values is $(10–15) \times 10^{-7} \text{ K}^{-1}$ (Fig. 2). It can be seen that the TCLE of borosilicate glasses with different RO contents depends not so much on the ionic

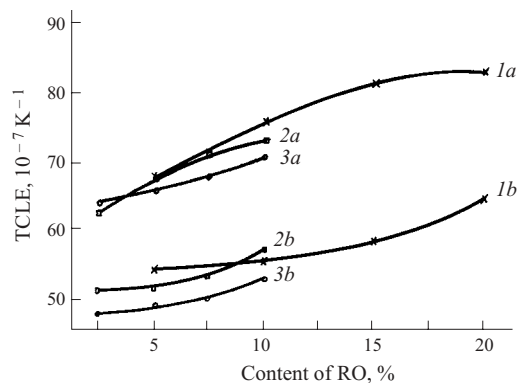


Fig. 2. Dependence of TCLE on content of BaO (1), SrO (2), and MgO (3): a) calculated values; b) experimental data.

radius of the modifier cation as on the structural state of the glass.

It is known that the softening temperature of glass t_s depends on the glass structure, the quantity of non-bridge bonds, and the strength of the cation-anion bond and is one of the most important parameters.

To study the effect of the composition of liquating phases on t_s , variations of the softening point in calcium- and zinc-bearing glasses were investigated (Fig. 3). The curve of the dependence of t_s on the composition has an inflection as well. With a CaO content equal to 15% or less, the glasses have a higher t_s than the compositions with 20% and more CaO.

In compositions containing up to 20% CaO the matrix is formed by the high-silica phase, which accounts for the higher t_s of glasses. Since the strength of the bond of the cations to oxygen in the specified phase is higher than in the boron-rich phase containing the major part of Ca^{2+} and Na^+ that have lower values of the single cation – oxygen anion bond, this leads to decreasing t_s .

It should be noted that t_s is higher in glasses with a high-silica matrix, which is expected, since high-silica glass is higher-melting and, accordingly, more viscous.

The curves shown in Fig. 3 have an inflection at a ZnO content of 20–25%, which indicates inversion of the phases. Glasses with a high-silica matrix typically have a higher t_s , which is related to the stronger force of the cation – anion bond in this phase. Changing over to glasses with a boron-rich matrix phases abruptly decreases the t_s .

The softening point of calcium-bearing glasses is slightly higher than that of zinc-containing glasses. This is due to a more intense fluxing effect of ZnO compared to CaO.

Thus, the softening temperature of liquating glasses in the calcium- and zinc-containing systems significantly depends on the distribution of liquating phases. In the case of inversion of phases, inflections are seen on the curves.

The dependences of the softening temperature of glasses on the content of bivalent metal oxides (SrO, MgO, and BaO) are also shown in Fig. 3.

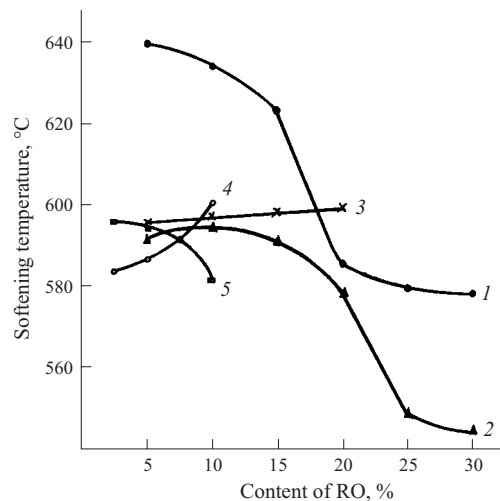


Fig. 3. Dependence of softening temperature of glasses on content of CaO (1), ZnO (2), BaO (3), MgO (4), and SrO (5).

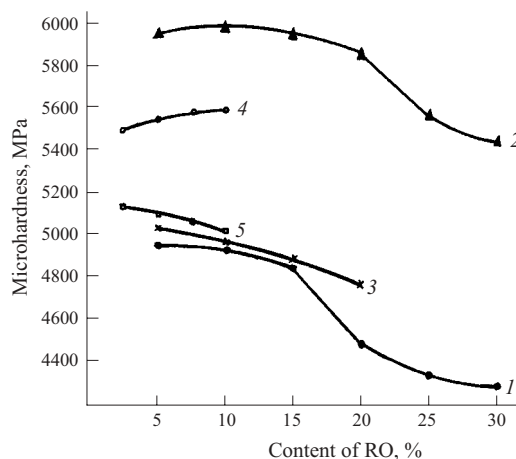


Fig. 4. Dependence of microhardness on the content of bivalent metal oxides: 1, 2, 3, 4 and 5) CaO, ZnO, BaO, MgO, and SrO, respectively.

Analyzing the data obtained, it can be concluded that the softening temperatures of experimental glasses containing MgO and BaO grows as their quantity increases; SrO decreases t_s , especially when its content is 5–10%.

The microhardness of glass is a complex function of its chemical composition, which depends on the structural state of glass and the type of chemical bonds.

It is established that the microhardness of calcium and zinc-bearing glasses decreases within the limits of 4950–4380 and 6000–5480 MPa, respectively. Two compositions ranges can be distinguished in Fig. 4., i.e., compositions with relatively high microhardness, in which the microhardness gradually decreases with increasing CaO and ZnO content, and compositions with lower microhardness, in which the values change smoothly as well depending on the composition. Between these two ranges there is an inflection corre-

sponding to 15 – 20% CaO and 20 – 25% ZnO. The higher microhardness is typical of glasses with a high-silica matrix, and the lower is observed in glasses with the matrix containing B_2O_3 , Na_2O , and CaO for calcium-bearing glasses and the matrix containing Na_2O , ZnO, and B_2O_3 for zinc-bearing glasses. Such distribution of microhardness values is quite natural, since ions in the high-silica phase are linked by stronger bonds, whereas the strength of bonds in the phase containing B_2O_3 is lower due to the large quantity of Ca^{2+} and Na^+ cations in the calcium-bearing system and Zn^{2+} and Na^+ in the zinc-bearing system.

The microhardness of glasses in the zinc-bearing system is slightly higher than that of the analogous glass compositions in the calcium-bearing system. This can be explained based on the data of A. A. Appen [2], who found that the microhardness of glass containing ions of bivalent metals grows with decreasing ionic radii of these metals. The Zn^{2+} ion, having a small ionic radius, imparts a higher microhardness to glass than the Ca^{2+} ion. However, experimental data show that despite the significant difference in the ionic radii, zinc-bearing glasses surpass only slightly calcium-bearing glasses in their microhardness.

The dependences of microhardness of glass on its content of SrO, MgO, and BaO are linear. The microhardness decreases with increasing content of SrO and BaO and its values are within intervals of 4920 – 4760 and 4859 – 4660 MPa, respectively. As for MgO, it produces the most perceptible increase in the microhardness of glass. In the investigated interval of MgO content the microhardness grows insignificantly and is equal to 5320 – 5550 MPa.

The density of glass depends on the type of its component oxides, the type of bonds between them, the structural lattice ordering, and the packing density of structural elements, and, on the whole, is a structure-sensitive property.

As was expected, this dependence has positive curvature. A certain decrease in density is observed under a prevailing quantity of the high-silica phase in calcium-containing glasses. This is due to the presence of 3-coordination boron in the specified liquation phase, which contributes to loosening the silicon-oxygen skeleton, whereas 4-coordination boron incorporates into the structural lattice of glass and strengthens it. As the quantity of 4-coordination boron in the

main phase rich in B_2O_3 increases, the density grows and amounts to 2360 – 2600 kg/m³.

This dependence in the zinc-containing system has positive curvature as well and has no singular points, which is typical of liquating compositions. Under a prevailing quantity of the high-silica phase containing boron in 3-coordination a certain decrease in density is registered. With increasing volume of the phase containing B_2O_3 , in which boron exists mostly in the tetrahedral coordination, the density of glass slightly increases. The system density for the range investigated is within an interval of 2370 – 2780 kg/m³.

As for introducing SrO, MgO, and BaO, the glass density depends on the ionic radius of the cation, whose increase increases density. Strontium-bearing glasses have density of 2380 – 2560 kg/m³, and barium and magnesium-bearing glasses have density of 2320 – 2380 and 2420 – 2750 kg/m³, respectively.

The chemical resistance of glasses also provides certain information regarding the glass structure. Furthermore, chemical resistance is one of the most important service properties with respect to glass application.

Determination of the chemical resistance of glass to water indicated that all the glasses investigated are water-resistant: their weight loss does not exceed 0.5%. The dependences of water resistance of glass on the content of modifier oxides are linear. An exception to this regularity are glasses of the calcium- and magnesium-bearing systems in which the curves exhibit inflections, which are presumably related to inversion of phases. No clear effect of the modifier cation radius on water resistance was determined, because of too low weight losses commensurable with the experimental error.

Thus, the studies performed have established the ambiguous effect of bivalent cations on the properties of borosilicate systems, which is determined by the ionic radius of the cation and by the structural state of glasses.

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